AMENDMENTS TO THE SPECTIFICATION

Please amend the paragraph on page 2 starting at line 7 as follows:

Ideally an organosilicon reagent for use in a cross-coupling reaction will have low molecular weight, be highly effective for cross-coupling, easy to synthesize, stable under chromatographic purification conditions, easily activated toward organic electrophiles, particularly organic halides, and converted to harmless (or at least less toxic) by-products. It is further desirable that the organosilicon reagent be compatible with a variety of functional groups and exhibit stereoselectivity in reaction.

Please amend the paragraph on page 3, starting at line 19 as follows:

The transferable group (T) can be selected from aromatic (including aryl and substituted aryl), substituted aromatic, heteroaromatic, olefinic, substituted olefinic, allylic, substituted allylic, acetylenic, substituted acetylenic, allenic, substituted allenic, an acyl group, and an alkyl including: cycloalkyl and heterocycloalkyl groups, and substituted alkyl groups, including perfluoralkyl groups. T groups can also contain one or more substituents (~~Rs~~ R's) that are protected from reaction during the cross-coupling reaction by an appropriate protective group, as is understood in the art.

Please amend the paragraph on page 4 which begins at line 1 as follows:

T groups specifically include, cyclopropyl groups, epoxy groups, vinyl groups, propenyl groups, butenyl groups, pentenyl groups, hexenyl groups, heptenyl groups, acetylenic groups, propargyl groups, aryl-substituted alkenyl groups, phenyl groups, naphthyl groups, thienyl, pyridinyl groups or acyl groups. All T groups can be substituted with one or more non-hydrogen ~~substituenets~~ substituents (~~Rs~~ R's), which can include among others halides, CN, and NO_2 groups.

Please amend the paragraph bridging pages 4 and 5 as follows:

The activating agent A^+Z^- for activating the organosilicon nucleophile is an anion source. Preferred anions are those that can function as a base as well as a nucleophile. Anions include F^-, OH^-, CN^-, N_3^-, HF_2^-, $H_2F_3^-$, H^-, RO^-, where R is an alkyl or aromatic (including an aryl) group, $(R)_3SiF_2^-$ where different ~~Rs~~ R's in the same anion can be the same or different and are alkyl groups or aromatic (including aryl) groups, e.g., $(CH_3)_3SiF_2^-$, $(Ph)_3SiF_2^-$; and $(R)_3Si\text{-}O^-$~~, where R's in the same anion can be the same or different and can be alkyl or aromatic (including aryl) groups~~. Anions can be provided as salts with any appropriate cation. Cations include K^+, Na^+, R_4N^+, Cs^+, $(R_2N)_3S^+$ (where R is aliphatic). The cation is typically selected to facilitate solubility of the activating agent in the selected reaction solvent.

Please amend the paragraph on page 5 which begins at line 19 as follows:

The cross-coupling reaction of this invention is compatible with a number of other reactions which can be used to form organosilicon nucleophiles that can then participate in the cross-coupling reaction. In certain cases, the reagents for the cross-coupling reaction can be combined with those for generating the organosilicon nucleophile, so that a one-pot protocol can be employed to ~~generated~~ generate desired cross-coupling products.

Please amend the paragraph on page 14 which begins at line 6 as follows:

The invention also provides reagent kits which combine a selected organosilicon nucleophile of formula **I** (and all other formulas illustrated above) carrying a selected transferable group T with an activating agent A^+Z^- and optionally also contains a catalysts which may be provided as a stable organic source of the Group 10 metal in combination with a selected ligand or mixture of ligands. Preferably, the catalyst and activating agent are selected to facilitate the cross- coupling of the organosilicon reagent included in the kit and may be optimized for use with a choice of organic electrophiles. The kit may further include instructions for carrying out the reaction. The kit may also

provide appropriate solvent and/or an appropriate reaction vessel for carrying out the reaction. In preferred embodiments, ~~kit~~ kits of this invention comprise an organosilicon cross-coupling reagent that is a silacyclobutane, a siloxane (linear, cyclic or branched) or a bis-silyl compound.

Please amend the paragraph on page 20 that begins on line 12 as follows:

Careful investigation of the reaction between **42** and iodobenzene showed that homocoupling of both these substrates (to generate **45** or **46**, for example) was a serious liability (entry 1, Table 3) (11, 19). Where no ligand was added both possible homocoupling products **45** and **46** were observed. To facilitate the transmetallation and eliminate the ~~cross-coupling~~ homocoupling, various additives were surveyed with ratio of ligand/palladium of 2.0. The additives examined (Table 3) cover a wide range of donor properties and steric bulk. While $(o\text{-tol})_3P$ (entry 2), $(C_6F_5)_3P$ (entry 3), and phosphite **48** (entry 9) suppressed the desired coupling, the other ligands such as tri(2-furyl)-phosphine (entry 4) and triphenylarsine (entry 5) and the bulky ligands such as tri(*tert*-butyl)phosphine (entry 6) (20) and tricyclohexylphosphine (entry 7) were effective in eliminating the homocoupling of arylsilanes and significantly suppressing the homocoupling of aryl iodides. Nevertheless, the desired cross-coupling was still rather sluggish. It was surprising that recently introduced ligand **47** (entry 8) did not inhibit the generation of **45** (21).

Please amend the paragraph on page 21 which begins on line 7 as follows:

Preliminary studies found fluorosilane **42** to be superior to chlorosilacyclobutane **40** in the cross-coupling reaction. Under the identical conditions noted above in ~~Table 6~~ Table 5 (THF/50°C), the reaction with the chlorosilacyclobutane **40** was not complete within 22 hours. By carrying out the reaction in refluxing THF, complete conversion could be observed within 16 hours (Table 6). However, at the elevated temperature, the amount of side product **45** increased to 11% with a $(t\text{-Bu})_3P$/Pd ratio of 2.2. The amount of **45** can be reduced to less than 5% when the ratio of $P(t\text{-Bu})_3$/Pd is increased to 4.0.

Please amend the paragraph on page 31 which begins on line 1 as follows:

A practical solution to this problem was conceived in the form of a one-pot protocol that would (1) obviate the need to isolate and purify the delicate silyl ether and siloxane and (2) improve the overall efficiency of the process. Thus, to streamline the procedure and minimize the formation of potentially deleterious byproducts, ~~tetramethyldisilazanem~~ tetramethyldisilazane (TMDS) was employed as the silylating agent. The one-pot process is discussed below.

Please amend the paragraph on page 31 which begins at line 11 as follows:

Subjecting the hydridosilane 84 and 2-iodotoluene to the reaction protocol optimized with silanols gave rise to only a small amount of coupling product along with 1,5-diphenyl-3-pentanone from reduction of dba. The evolution of a gas when the silane was mixed with TBAF suggested that the silyl hydride was being ~~hydrolyzes~~ hydrolyzed. It is well-known that hydrolysis or alcoholysis of silyl hydrides can be catalyzed by fluoride ion at room temperature to liberate hydrogen gas. Thus, it appeared that the coupling product observed could be the result of silanol generated *in situ* from the silyl hydride.

Please amend the paragraph bridging pages 37 and 38 as follows:

The results of a survey of bases and solvents using (1-heptenyl)dimethylsilanol **(E)-21** and 1- iodonaphthalene are collected in Table 20. Whereas the lithium silyloxide was unreactive, the sodium salt, generated with NaH in THF clearly manifested the feasibility of this new process (entries 1-4). 2.0 equiv of base was needed for complete conversion, which was then used throughout. The reaction is considerably faster in DMF and DME. Other sodium bases (i.e., NaOt-Bu) were less effective promoters. The use of potassium hydride had a dramatic effect on the rate giving complete conversion within 15 in DME. Finally, potassium *tert*-butoxide was also able to promote the reaction and gave the highest yield despite the having the lowest rate of coupling. Weaker bases, such as K_2CO_3 and K_3PO_4 were ineffective. In all cases examined the reaction was shown to be

highly stereospecific. ~~Sheeme~~ Scheme11 illustrates reaction of vinyl silanols with aryl iodides in the presence of bases such as hydride.

Please amend the paragraph on page 39which begins at line 11 as follows:

The initial development of a one-pot protocol focused on the Pt-catalyzed hydrosilylation event. To optimize the hydrosilylation, the reaction of 1-heptyne with diisopropylchlorosilane was studied and the results were evaluated by directly carrying out the Pd-catalyzed cross-coupling (THF, 1.0M TBAF (2 equiv.), $Pd(dba)_2$ (5mol%), RT, 10 min.) with 1-iodonaphthalene. Hydrosilylation of 1-heptyne with diisopropylchlorosilane in the presence of H_2PtCl_6 (<0.1 mol %) at 50 °C for 30 min, followed by treatment with TBAF, $Pd(dba)_2$, and 1-iodonaphthalene gave incomplete coupling (70-80% conversion). No other isomeric, cross-coupling products ((Z)-**169a** or 170a) were observed by GC analysis. However, all attempts to improve the conversion failed. Consequently, a survey was performed to screen other silane sources and Pt catalysts for their activity and stereoselectivity in this transformation. Orienting experiments revealed that the regio- and stereoselectivity was strongly affected by the structure of silane. In the presence of Speier's catalyst, tetramethyldisiloxane, tetramethylcyclotetrasilioxane, and methyldiethoxysilane can participate in the hydrosilylation/cross-coupling reaction smoothly as evidenced by the complete consumption of 1-iodo naphthalene after 10 min. However, a small amount of the isomer **170a** (12-16%) resulting from regio-reversed hydrosilylation was observed. To improve the hydrosilylation regioselectivity, tetraisopropyldisiloxane was used, but only a trace of cross-coupling product was observed even after extended reaction time or at elevated reaction temperatures. Diethylethoxysilane was then examined as a compromise between reactivity and selectivity. Surprisingly, this silane gave the poorest results; the regioselectivity was worse than with the methylsilanes, and the conversion was below about 60%.

Please amend the second paragraph on page 45 which begins at line 9 as follows:

Analytical capillary gas chromatography (GC) was performed using a Hewlett Packard 5890 Series II gas ~~chromatographs~~ chromatograph fitted with a flame ionization detector (H_2 carrier gas, 1 mL/ min) and an HP- 5 (50- m, 0.2 mm) cross- linked phenyl methyl silicone capillary column. The injector temperature was 225 °C, the detector temperature was 300 °C. Oven temperature and head pressures specified. Retention times (t_R) and integrated ratios were obtained ~~form~~ from Hewlett Packard 3393A integrators.

Please amend the fourth paragraph on page 45, which starts at line 18 as follows:

The solvents used in reactions were reagent grade and distilled from the indicated drying agents under a nitrogen atmosphere: acetonitrile: CaH_2, tetrahydrofuran (THF):and diethyl ether ~~(Et_2O~~ (Et_2O): sodium metal/benzophenone ketyl. The solvents used for extraction and chromatography were technical grade and distilled from the indicated drying agents: hexane, pentane, dichloromethane (CH_2Cl_2): ($CaCl_2$); ethyl acetate:K_2CO_3. Unless otherwise noted, all nonaqueous reactions were performed in oven-and /or flame-dried glassware under an atmosphere of dry nitrogen.

Please amend the paragraph on page 90 that begins on line 3 as follows:

Solutions of tetrabutylammonium fluoride (TBAF) in THF (1.0 M) employed in all descriptive runs were prepared from colorless crystalline tetrabutylammonium fluoride trihydrate (Fluka). Tetramethyldisiloxane was from Lancaster and directly used without further purification. Phenylacetylene (Aldrich) was distilled prior to use. All other alkynes, heptyne, 4- pentyn- 1- ol (GFS) and 2- phenyl- 3- butyn- 1- ol (Fluka) were directly used without further purification. All the commercial halide reagents (Aldrich, ACROS) were purified by distillation or column chromatography prior to use. Allylpalladium chloride dimer [allylPdCl] 2 was purchased from ACROS. ~~Platium~~

Platinum(0)- 1,3- divinyl- 1,1,3,3,- tetramethyldisiloxane complex, solution in xylene was purchased from Aldrich.

Please amend the paragraph on page 90 that begins at line 12 as follows to clarify the last words of the paragraph which were partially obscured in the application as filed.:

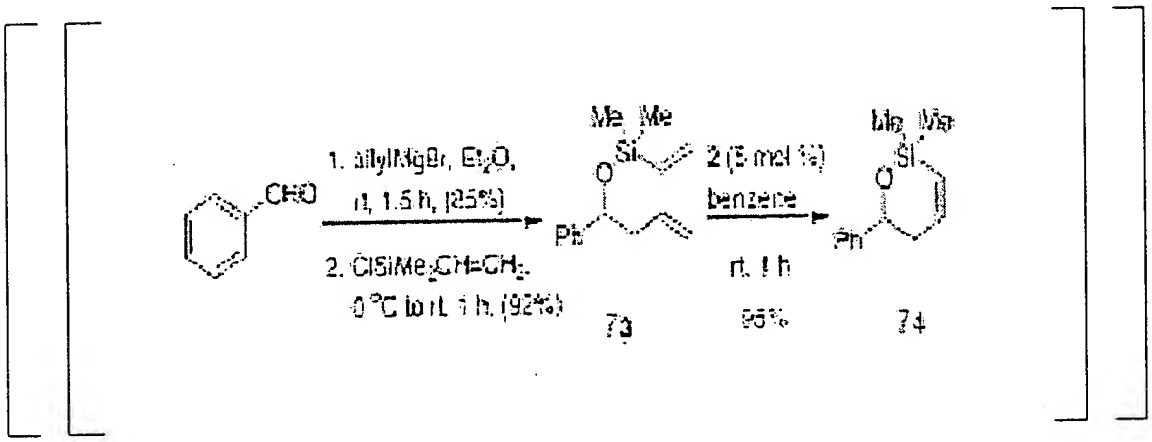
t- Bu 3 P- Pt(0) complex was prepared according to the literature procedure [1] : t- Bu 3 P (32 mg, 0.158 mmol) (Strem Chemicals) was dissolved in platinum(0)- 1,3- divinyl- 1,1,3,3-tetramethyldisiloxane complex (1.5 mL solution in xylene, Aldrich). The mixture was stirred at 65 °C (oil bath) for 5 min and then was slowly cooled to rt. This solution could be stored under N_2 in the freezer indefinitely.

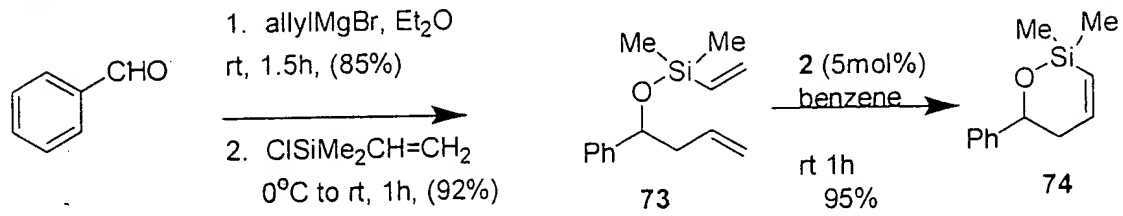
Please amend the paragraph at page 98 which begins at about line 10 (the last paragraph on the page) as follows:

Following General Procedure II, a mixture of $KOSiMe_3$ (570 mg, 4.0 mmol, 2.0 equiv), (Z)-21 (379 mg, 2.2 mol, 1.1 equiv), iodobenzene (1.0 mmol) and $Pd(dba)_2$ (58 mg, 0.1 mmol, 0.05 equiv) was stirred at room temperature for 7.5 h, and then was filtered through SiO_2. Purification by column chromatography (RP C18, MeOH.H_2O, 9/1) and Kugelrohr distillation afforded 298 mg (86%) of (Z)-~~154b~~ **154b** as colorless oil. ~~The spectroscopic data matched those from~~

Please amend the paragraph at page 27, beginning at line 10 to replace the formula, as follows:

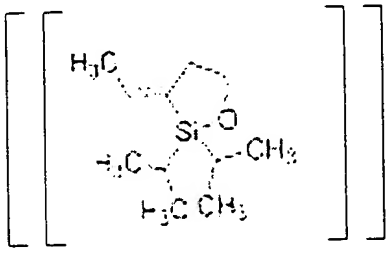
The cyclic silyl siloxane 74 was prepared by ring-closing metathesis (RCM) using the molybdenum carbene complex 72 $[(CF_3)_2MeCO]_2Mo(=CHCMe_2Ph)(=NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)$ developed by Schrock et al.(33):

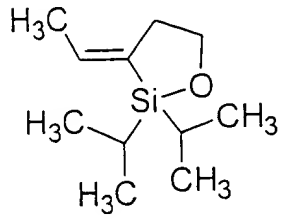




Please amend the paragraph bridging pages 28 and 29 as follows:

The cyclic siloxane **78** was formed by intramolecular hydrosilyation as will be discussed below.



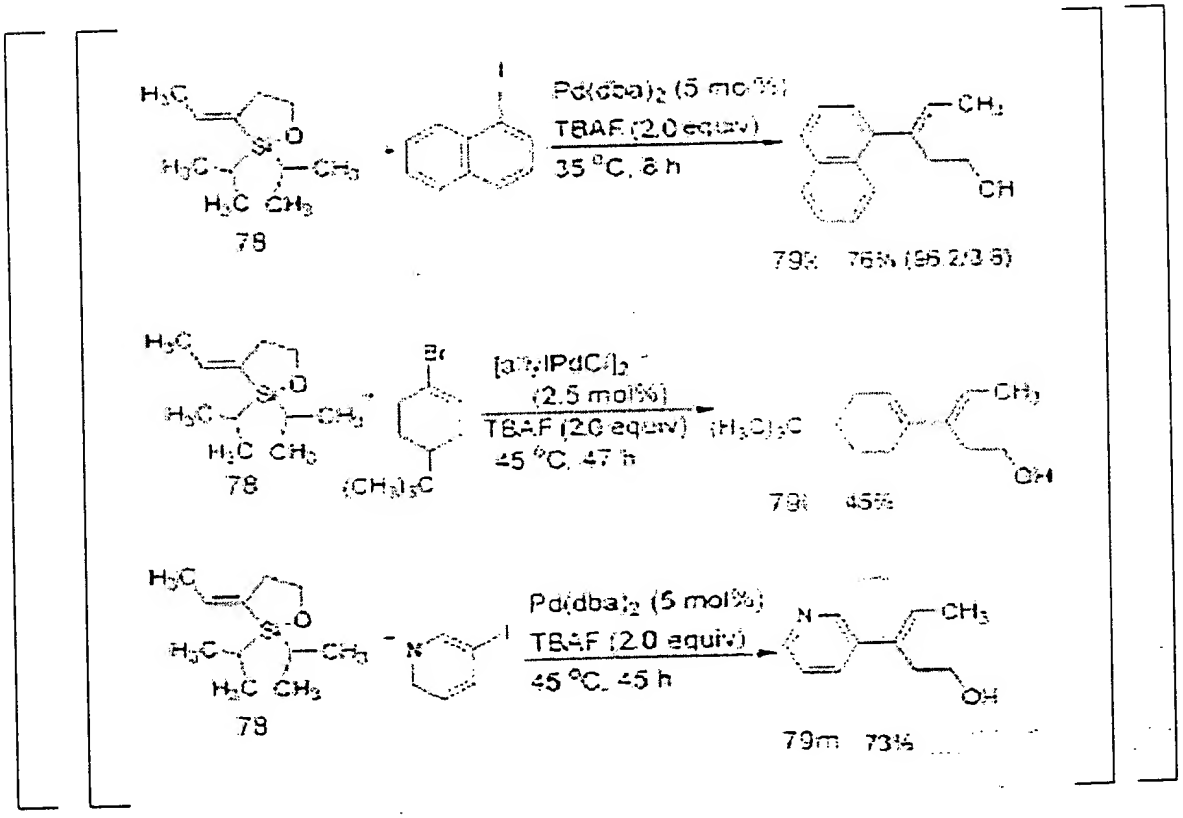


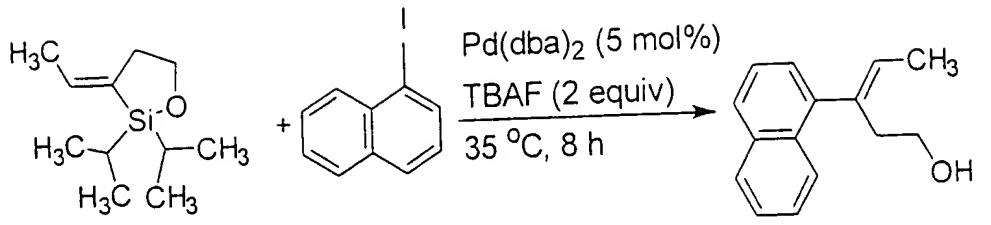
78

Siloxane **78** was dissolved in 2.0 equiv of a 1.0 M solution of TBAF in THF, followed by the addition of iodobenzene and 5 mol % of Pd(dba)2. The siloxane did undergo the coupling process, however, at a significantly reduced reaction rate compared to the related silanols. Moreover, the reaction mixture was contaminated with a substantial amount of biphenyl (the product of self-coupling of iodobenzene), and thus the yield of the cross-coupling product was attenuated. The addition of various ligands or decreasing the amount of Pd(0) did not meaningfully improve the results. It was found, however, that adding the iodide in portions satisfactorily suppressed the formation of biphenyl and correspondingly improved the yield of the desired coupling product. The portionwise addition of the iodide proved to be effective in reducing the amount of homocoupling byproduct in most cases. For a few, very slow reacting substrates, even this expedient was not helpful.

Please amend the paragraph on page 30 beginning at line 1 to replace the equations as follows:

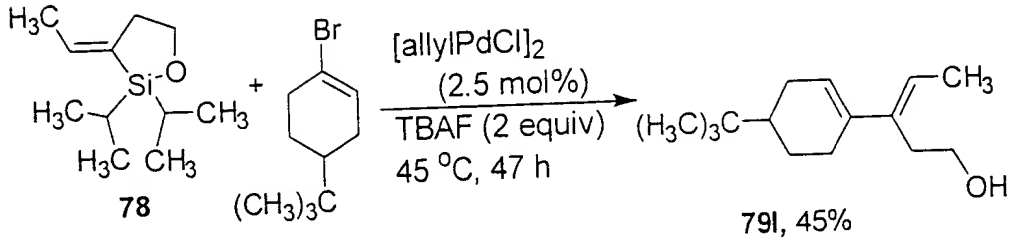
This variant of the coupling reaction is not limited to benzene derivatives. For instance, 1-iodonaphthalene, 1-bromo-4-tert-butyl-1-cyclohexene (an unactivated vinyl bromide), and 3-iodopyridine reacted with **78** to give the expected products **79k**, **79l**, and **79m**, respectively, in reasonable to good yield:





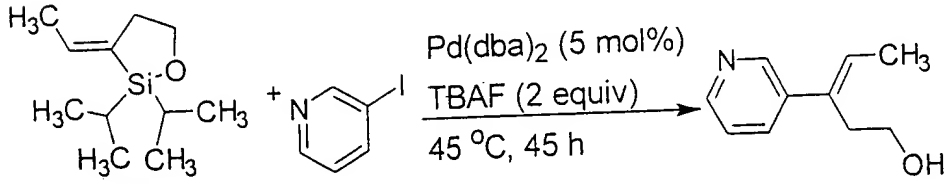
78

79k, 76% (96.2/3.8)



78

79l, 45%

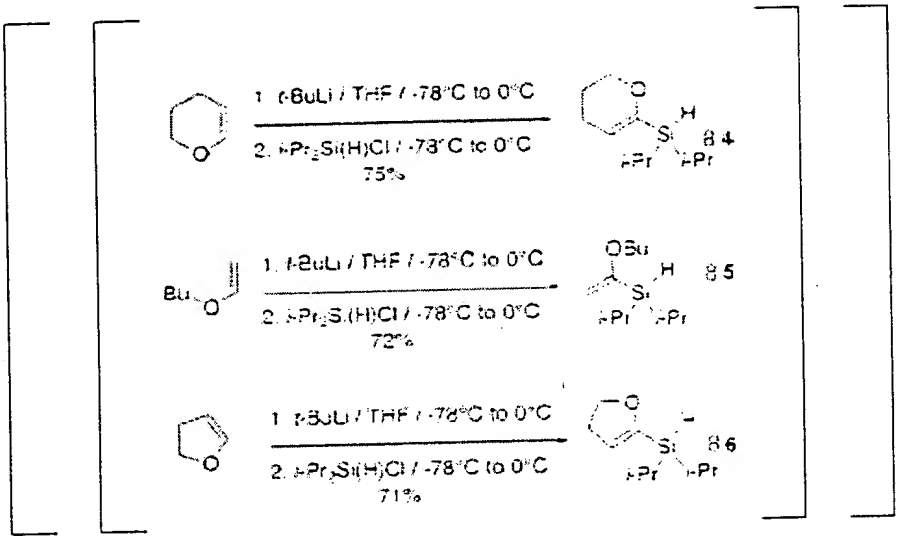


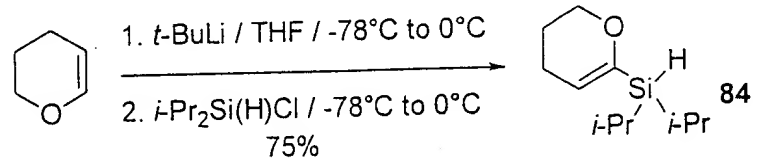
78

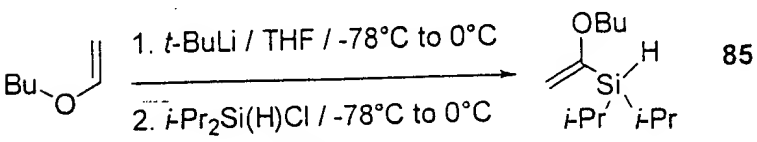
79m, 73%

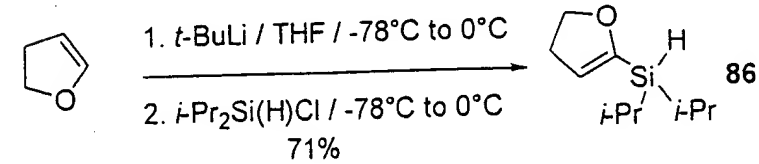
Please amend the paragraph on p age 31 beginning at line 7 to replace the equations:

Silyl hydrides are useful precursors for cross-coupling, particularly in those cases where the hydroxyl functionality would not be tolerated. Scheme 7B illustrates the reactions of silyl hydrides with aryliodides. Silyl hydrides were prepared as exemplified for hydrides **84-86**:



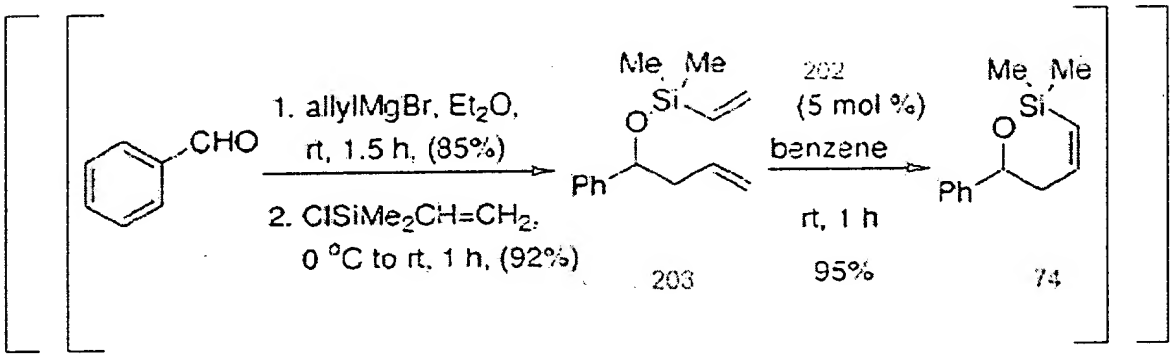


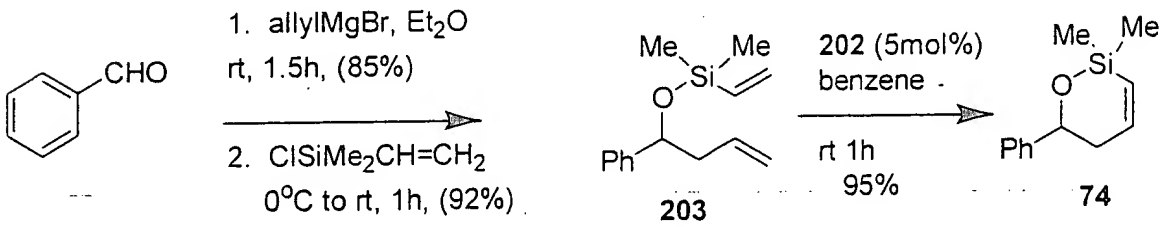




Please amend the paragraph on page 42 beginning at line 4 to replace the equation as follows:

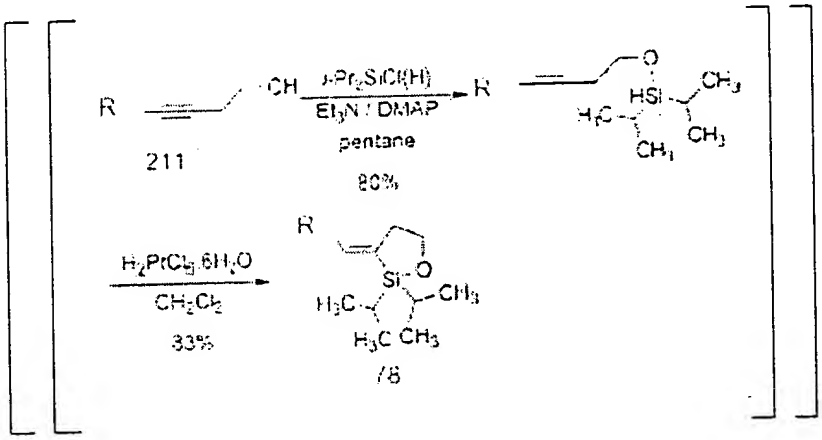
To test the feasibility of the overall transformation, combining the two types of reaction the vinylsilyl ether, **203**, was prepared as a starting material for RMC by addition of allylmagnesium bromide to benzaldehyde followed by silylation with commercially available chlorodimethylvinyl-silane. Initial studies on the RCM reaction of **203** using the Grubbs alkylidene complex none of the desired ring-closure product **74**, was observed. All variations in conditions, including change of solvent and/or temperature were unsuccessful. Substrate **203** did undergo the RCM process when the molybdenum complex **202** was used as the catalyst. After careful optimization a near quantitative yield of **74** was obtained with 5 mol % of **202** in benzene at ambient temperature.

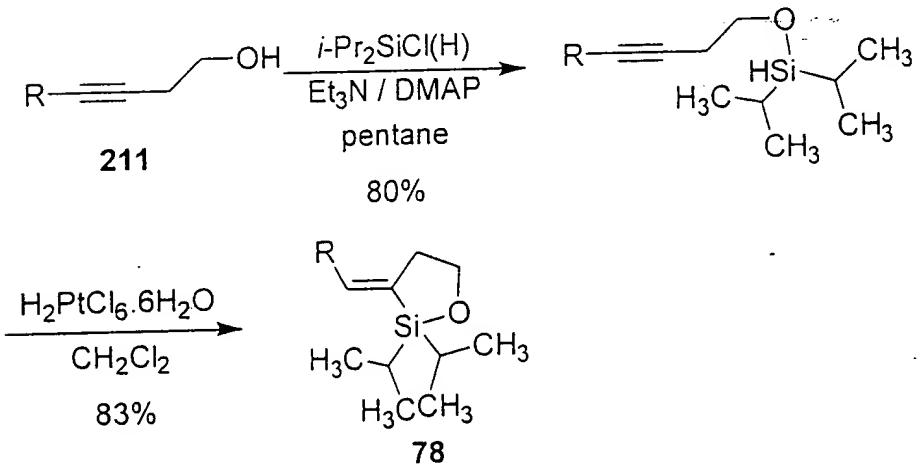




Please amend the paragraph on page 43 beginning at line 14 as follows:

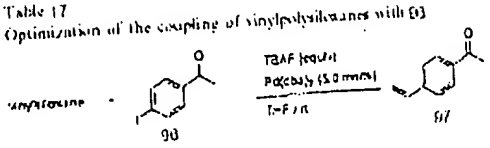
In particular, the cyclic siloxane **78** (where R is CH_3-) derived from 3-pentyn-ol (**211**, where R is CH_3-) was examined to illustrate the combination of intramolecular hydrosilylation and cross-coupling of this invention. Silylation of the alkynol with diisopropylchlorosilane provided a silyl ether in good yield which was then subjected to intramolecular hydrosilylation using a catalytic amount of Speier's catalyst:





Please replace the paragraph containing Table 17 on page 133 of the specification as follows:

Table 17
Optimization of the coupling of vinylpolysiloxanes with 98

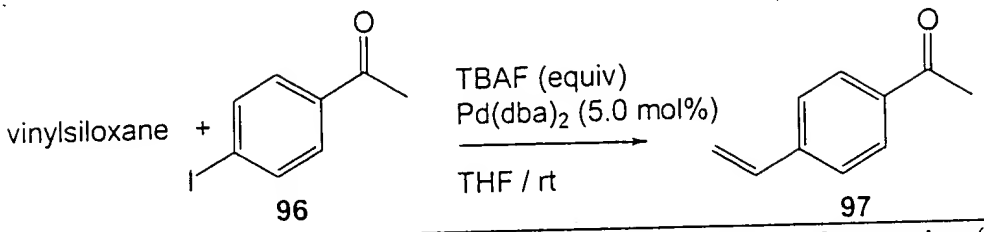


Entry	Vinylsiloxane (equivalents)	TBAF (equivalents)	Time (min)	Conversion (%)[a]
1	92 (1.2 eq)	2.0	10	100 (88)
2	93 (1.2 eq)	2.0	10	100 (85)
3	94 (1.2 eq)	2.0	10	100 (89)
4	95 (1.2 eq)	2.0	10	78
5	95 (1.5 eq)	2.0	10	94 (81)
6	95 (1.5 eq)	3.0	10	93 (83)

[a] The numbers in parentheses are isolated yields from 2.0 mmol scale experiments.

Table 17

Optimization of the coupling of vinylpolysiloxanes with 96



96 97

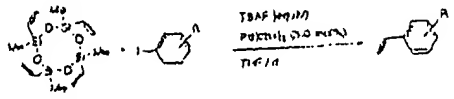
Entry	Vinylsiloxane (equivalents)	TBAF (equivalents)	Time (min)	Conversion (%)
1	92 (1.2/4)	2.0	10	100 (88)
2	93 (1.2/3)	2.0	10	100 (85)
3	94 (1.2/3)	2.0	10	100(89)
4	95 (1.2/6)	2.0	10	78
5	95 (1.5/6)	2.0	10	94 (51)
6	95 (1.5/6)	2.0	10	93 (53)

*The numbers in parentheses are isolated yields from 2.0 mmol scale experiments.

Please amend the specification at page 134 to replace Table 18 as follows:

Table 18

Cross-coupling of 92 with acyl halides[a]

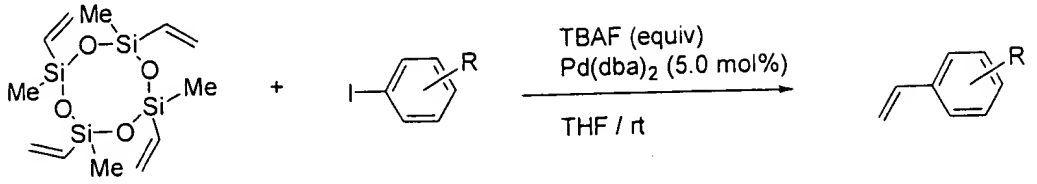


92

Entry	Aryl R	92 (equivalents)	TBAF (equivalents)	Time (min)	Product	Yield (%)
1	4-COMe 93	1.2:1	2.0	10	97	88
2[b]	4-COMe 93	1.2:1	2.0	10	97	90
3	4-COOEt 95	1.2:1	2.0	10	99	85
4[b]	4-COOEt 95	1.2:1	2.0	60	99	83
5	4-COMe 109	1.5:1	3.0	240	101	46
6[c]	4-COMe 109	1.5:1	3.0	360	101	63
7	3-NO_2 102	1.2:1	2.0	10	103	87
8[b]	3-CH_2OH 104	1.25:1	2.0	480	105	59
9[b]	2-OMe 106	1.5:1	3.0	24 h	107	72
10[b]	2-COOMe 108	1.2:1	2.0	480	109	83
11	1-naphthyl 110	1.2:1	2.0	180	111	64

[a] All the reactions were conducted under argon on 2.0 mmol scale.
[b] 4-Methoxyacetophenone added last over 45 min at 50°C.
[c] 1 mol% $Pd(dba)_2$ loading.
[d] 10 mol% $AsPh_3$ added.

Table 18
Cross-coupling of **92** (D_4^v) with aryl iodides[a]



92

Entry	Aryl R	92 (equiv.)	TBAF (equiv)	Time (min)	Product	Yield (%)
1	4-COMe (**96**)	1.2/4	2.0	10	**97**	88
2	4-COMe (**96**)	1.2/4	2.0	10	**97**	80
3	4-COOEt (**98**)	1.2/4	2.0	10	**99**	85
4	4-COOEt (**98**)	1.2/4	2.0	60	**99**	83
5	4-OMe (**100**)	1.5/4	3.0	240	**101**	46
6	4-OMe (**100**)	1.5/4	3.0	360	**101**	63
7	3-NO_2 (**102**)	1.2/4	2.0	10	**103**	87
8	3-CH_3OH (**104**)	1.2/4	2.0	480	**105**	59
9	2-OMe (**106**)	1.5/4	3.0	24h	**107**	72
10	2-COOMe (**108**)	1.2/4	2.0	480	**109**	83
11	1-naphthyl-I (**110**)	1.2/4	2.0	180	**111**	64

[a] All the reactions were conducted under argon on 2.0 mmol scale.
[b] 4-Iodoacetophenone added last over 45 min at <30°C.
[c] 1 mol% $Pd(dba)_2$ loading.
[d] 10 mol% $AsPh_3$ added.